

1 **NONISOCYANATE POLYURETHANE MATERIALS,**
2 **AND THEIR PREPARATION FROM EPOXIDIZED SOYBEAN OILS**
3 **AND RELATED EPOXIDIZED VEGETABLE OILS,**
4 **INCORPORATION OF CARBON DIOXIDE INTO SOYBEAN OIL, AND**
5 **CARBONATION OF VEGETABLE OILS**

6
7 *Cross-Reference to Related Applications*

8 Priority is claimed to U.S. provisional application 60/447,729 filed February 19, 2003,
9 which is incorporated herein by reference.

10
11 **DESCRIPTION**

12 *Field of the Invention*

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14 The present invention generally relates to network polymers, more specifically, to
15 methods of producing nonisocyanate polyurethane networks, and the network nonisocyanate
16 polyurethanes produced thereby.

17
18 *Background of the Invention*

19
20 Conventionally, polyurethanes have been made using, as reagents, toxic isocyanates
21 which are themselves produced from phosgene, which is even more dangerous.

22 Subsequently, a newer field emerged, of producing polyurethanes without using
23 isocyanates, and certain nonisocyanate polyurethanes (NIPUs) have been provided. For example,
24 most recently, in U.S. Patent No. 6,120,905, titled "Hybrid Nonisocyanate Polyurethane Network
25 Polymers and Composites Formed Therefrom," issued September 19, 2000 to Figovsky, there are
26 discussed certain nonisocyanate polyurethane networks which are said to be produced based on
27 reactions between oligomers comprising terminal cyclocarbonate groups and oligomers
28 comprising terminal primary amine groups. Such nonisocyanate production methods have a
29 general safety advantage over production methods which typically depend on toxic isocyanates

and, in turn, are themselves produced from dangerous phosgene. Additionally, nonisocyanate polyurethanes also address certain desired applications better than isocyanate polyurethanes, such as in composite matrix materials or when chemical resistance to aqueous solutions of acids and alkalies is wanted. However, in the case of Figovsky's patent, it will be appreciated that there still is dependence on a main starting material that is a commercial petrochemical, such as a glycidyl ether of diaminophenol with tetraethyl ammonium chloride (Example 1-1). The methods of Figovsky (and of others) rely on commercial petrochemical starting materials to make nonisocyanate polyurethane networks.

It will be appreciated that polyurethane networks are just one of many kinds of polymers that have been developed over the years.

Speaking with regard to polymers generally, polymers prepared from renewable natural resources have become increasingly important because of their low cost, ready availability, and possible biodegradability. Kaplan, D. L., *Biopolymers from renewable resources*, Springer-Verlag (New York) 1998.

Vegetable oils are renewable triglyceride oils based on different fatty acids with varying degrees of unsaturation. Their conversion to useful intermediates for polymeric materials is significant scientifically, economically, and environmentally.

Soybean oil (SBO) is the most readily available and one of the lowest cost vegetable oils in the world. Markley, K.S., *Soybean and soybean products*, vol. 2, Interscience (New York), 1951; Soy-based paint and coating technical fact sheet, United Soybean Board, 1997.

In the past decade, much effort has been dedicated to producing SBO-based polymeric materials. Recently, Wool and coworkers, as well as others, have reported the use of SBO and other triglyceride oils to synthesize several different types of monomers which can promote polymeric networks with a wide range of physical properties. Khot, S. N., Lascala, J. J., Can, E., Morye, S. S., Williams, G. I., Palmese, G. R., Kusefoglu, S. H., Wool, R. P., *J Appl Polym Sci*, 2001, 82, 703; Wool, R., Kusefoglu, S., Palmese, G., Khot, S., Zhao, S., Zhao, R., U.S. Patent No. 6,121,398 (2000).

The generation of these monomers was possible by the use of different functionalities present in the triglyceride molecules, i.e., double bond, the allylic carbon, the ester group and the

1 carbon alpha to the ester group, which can be transformed into other reactive polymerizable
2 moieties.

3 One of the major interests of other researchers has been investigation into the possibility
4 of converting SBO into polyols for use in the polyurethane industry. Petrovic and coworkers
5 have used epoxidized soybean oil (ESBO) to develop a range of polyols which can then be
6 reacted with isocyanates to produce polyurethanes with useful properties. Guo, A., Cho, Y.,
7 Petrovic, Z. S., J Polym Sci A (2000), 38, 3900; Petrovic, Z. S., Guo, A., Zhang, W., J Polym Sci
8 A (2000), 38, 4062; Guo, A., Javni, I., Petrovic, Z., J Appl Polym Sci (2000), 77, 467; Javni, I.,
9 Petrovic, Z. S., Guo, A., Fuller, R., J Appl Polym Sci (2000), 77, 1723; Javni, I., Zhang, W.,
10 Petrovic, Z. S., Polym Mat Sci Eng (2002), 86, 387; Petrovic, Z. S., Zhang, W., Zlatanic, A.,
11 Lava, C. C., Polym Mat Sci Eng (2002), 86, 377; Guo, A., Demydov, D., Zhang, W., Petrovic,
12 Z.S., Polym Mat Sci Eng (2002), 96, 385.

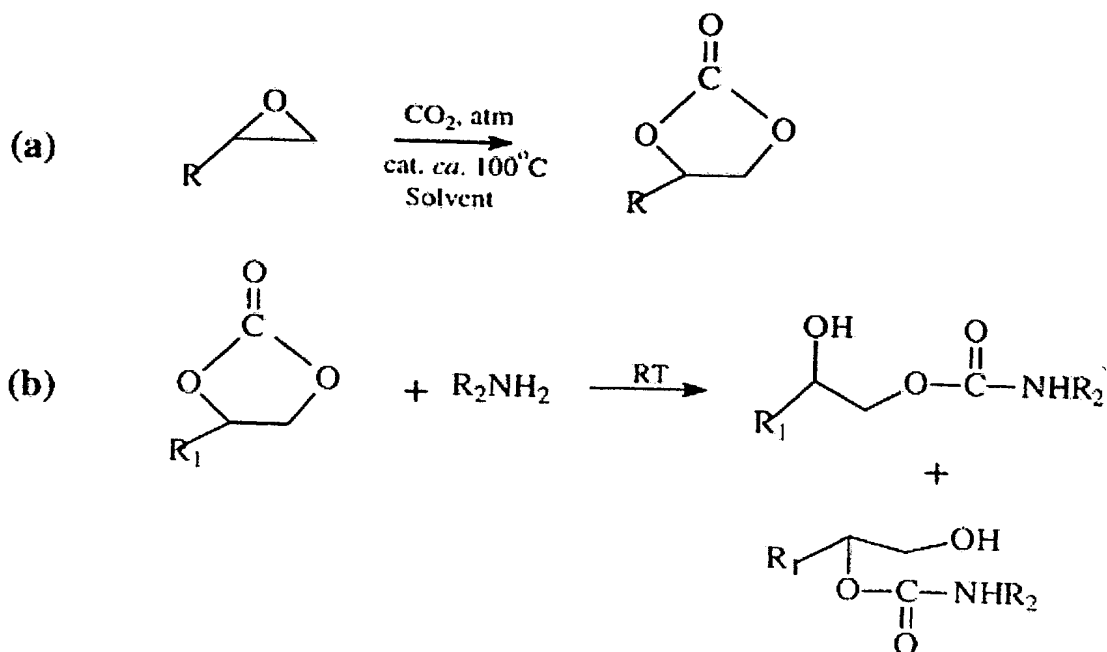
13 ESBO is the result of epoxidation of the double bonds of the SBO triglycerides with
14 hydrogen peroxide, either in acetic acid or in formic acid. Swern, D., Billen, G. N., Findley, T.
15 W., Scanlan, J. T., J Am Chem Soc (1945), 67, 1786; Meffert, A., Kluth, H., U.S. Patent No.
16 4,886,893 (1989); Rangarajan, B., Havey, A., Grulken, E. A., Culnan, P.D., J Am Oil Chem Soc
17 (1995), 72, 1161. ESBO is industrially available in large volumes at a reasonable cost.

18 Much attention has also been paid to carbon dioxide as the most inexpensive and readily
19 available carbon resource. Inoue, S., Organic and bioorganic chemistry of carbon dioxide, in
20 Inoue, S., Yamazaki, N., eds., Kodonsha Ltd.: Tokyo (1982).

21 Active investigation of the incorporation of carbon dioxide into organic molecules has
22 been carried out from an economical and environmental point of view. Among many studies of
23 chemical carbon-dioxide fixation, the reaction of oxiranes and carbon dioxide to provide the five-
24 membered cyclic carbonate has received much attention because of its simple reaction, high
25 yield, and harmless nature of the reagents. Kihara, N., Hara, N., Endo, T., J Org Chem (1993),
26 58, 6198; Iwasaki, T., Kihara, N., Endo, T., Bull Chem Soc Jpn (2000), 73, 713.

27 The reaction can be performed with the help of a catalyst under atmospheric pressure at
28 about 100° C (Scheme (a), below). Scheme (a) shows the reaction of oxirane with carbon
29 dioxide. A large number of catalyst systems have been reported in the literature for this reaction;

among them the alkali metal halides, quaternary ammonium halides, and polystyrene bound quaternary ammonium salts are the most effective. Kihara et al., *supra*; Iwaski et al., *supra*; Nishikubo, T., Kameyama, A., Yamashita, J., Tomoi, M., Fukuda, W., *J Polym Sci A* (1993), 31, 939.



As has been demonstrated, five-membered cyclic carbonates readily react with primary amines at room temperature to yield 2-hydroxyethylurethane quantitatively (Scheme (b), above). Kihara, N., Endo, T., *Makromol Chem* (1992), 193, 1481.

Furthermore, recently Endo and coworkers, as well as others, have reported the polyaddition reaction of bifunctional cyclic carbonates with aliphatic diamines to give polyhydroxyurethanes, often commonly called "nonisocyanate polyurethanes" (NIPUs). Kihara, N., Endo, T., *J Polym Sci A* (1993), 31, 2765; Kihara, N., Kushida, Y., Endo, T., *J Polym Sci A* (1996), 34, 2173; Steblyanko, A., Choi, W., Sanda, F., Endo, T., *J Polym Sci A* (2000), 38, 2375; Kim, M.-R., Kim, H.-S., Ha, C.-S., Park, D.-W., Lee, J.-K., *J Appl Polym Sci* (2001), 81, 2735; Tomita, H., Sanda, F., Endo, T., *J Polym Sci A* (2001), 39, 851 & 860; Figovski, O., L., U.S. Patent No. 6,120,905 (2000); Gabriel, R., Piotrowska, A., *Polymer* (2002), 43, 2927.

They showed that one of the advantageous features of this polyaddition was its high

chemoselectivity, i.e., it could be prepared in the presence of water, alcohol, and esters.

Summary of the Invention

Polymers made from renewable natural resources rather than commercial petrochemicals are highly desirable. The present invention provides novel carbonated vegetable oils (of which a preferred example is a carbonated soybean oil) and polymeric networks made from natural resources (such as, preferably, epoxidized vegetable oils, most preferably of which are mentioned epoxidized soybean oils), of which nonisocyanate polyurethane networks are mentioned as a most preferred example. The present invention also provides novel methods of making polymeric networks (such as, e.g., polyurethane networks). Also, the present invention provides novel methods of treating natural resources (such as, e.g., oils, such as, preferably, vegetable oils (e.g., soybean oil, linseed oil, sunflower oil, palm oil, etc.), most preferably, soybean oil.

In a preferred embodiment, the present invention provides novel products that are carbonated natural oils, preferably carbonated vegetable oils, such as carbonated soybean oil, carbonated linseed oil, etc., of which a particularly preferred example is a carbonated soybean oil (CSBO).

The present inventors have recognized the benefits of carbonating a vegetable oil (such as soybean oil, linseed oil, palm oil, sunflower oil, etc.), and have discovered that a carbonated product (such as a carbonated soybean oil) of such a natural starting material may be made into a polymeric network. In a preferred embodiment, the present invention provides a monomeric functionalized CSBO, from which may be subsequently polymerized a nonisocyanate polyurethane network. The present inventors provide novel methods for producing monomeric functionalized CSBO products and polyurethane network products.

List of Figures

Figures 1a-c show FT-IR spectra, of, respectively: epoxidized soy bean oil (ESBO) (Figure 1a), carbonated soybean oil (CSBO) (Figure 1b) and a reaction product of CSBO and *n*-

1 butylamine (Figure 1c).

2 Figures 2a-b show GPC profiles, of, respectively: ESBO (Figure 2a), and CSBO
3 (Figure 2b).

4 Figure 3 shows TGA profiles of mass loss with temperature for ESBO and CSBO.

5 Figure 4 is a graph of variation of sol fraction as a function of the mass ratio of amine
6 functionality to cyclic carbonate.

7 Figures 5A-5B are graphs of dynamic mechanical analysis for various nonisocyanate
8 polyurethane (NIPU) samples, plotting temperature versus $\tan \delta$ in Figure 5A, and temperature
9 versus storage modulus (E') in Figure 5B.

10 Figure 6 is a graph of tensile stress experiments performed on NIPU samples at ambient.

11 Figure 7a-b are reactions according to the present invention, with a schematic (a) of the
12 reaction, according to an embodiment of the invention, of epoxidized soybean oil (ESBO) with
13 carbon dioxide to form carbonated soybean oil (CSBO), and a schematic (b) of the model
14 reaction, according to an embodiment of the invention, of CSBO with *n*-butylamine.

15 16 DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

17
18 The present invention provides a method of converting an epoxide ring to a five-
19 membered cyclic carbonate ring, comprising a step of: reacting a starting material that contains
20 an epoxide ring with carbon dioxide, wherein the epoxide ring is converted to a five-membered
21 cyclic carbonate ring. Such a starting material containing an epoxide ring(s) is particularly
22 preferred for use when contained in a natural resource, especially a non-hazardous natural
23 resource, of which epoxidized vegetable oils are preferred examples, with epoxidized soybean oil
24 (ESBO) being a particularly preferred example.

25 Thus, in a preferred embodiment, the present invention provides a method of making a
26 monomeric functionalized oil, comprising the step of: carbonating an epoxidized vegetable oil,
27 wherein a carbonated vegetable oil is produced.

28 As the vegetable oil, there may be used, e.g., soybean oil (SBO), linseed oil, palm oil,
29 sunflower oil, or other vegetable oils, of which soybean oil is a particularly preferred example.

1 Vegetable oils are commercially available, and may even be purchased at a grocery store. Using
2 such a non-hazardous starting material is beneficial. Epoxidization of a vegetable oil may be
3 accomplished by appropriate chemical derivatization. Alternately, vegetable oils may be
4 purchased in epoxidized form.

5 Among the carbonated vegetable oils that may be produced according to the present
6 invention are vegetable oils containing cyclic carbonate groups, of which carbonated soybean oil
7 (CSBO) is mentioned as a preferred example of a novel carbonated vegetable oil.

8 The carbonating according to the present invention may be achieved by reacting the
9 epoxidized vegetable oil (such as ESBO) with carbon dioxide (gaseous form). Carbon dioxide is
10 readily commercially available. Most preferably, a catalyst is present for the carbonation. A
11 particularly preferred example of a catalyst to use during carbonation is tetrabutylammonium
12 bromide (TBAB). Other examples of catalysts tested are mentioned in the Experiment, below.
13 Advantageously, the present invention provides for converting the epoxidized vegetable oil to
14 carbonated oil without any significant side reactions occurring, such as, for example, when
15 ESBO is converted to CSBO.

16 Such novel methods according to the present invention provide a variety of novel
17 products, including, e.g., a modified vegetable oil comprising a carbonated vegetable oil (such as
18 carbonated soybean oil, etc.); a modified vegetable oil comprising: a vegetable oil containing
19 cyclic carbonate groups (such as a modified soybean oil); etc.

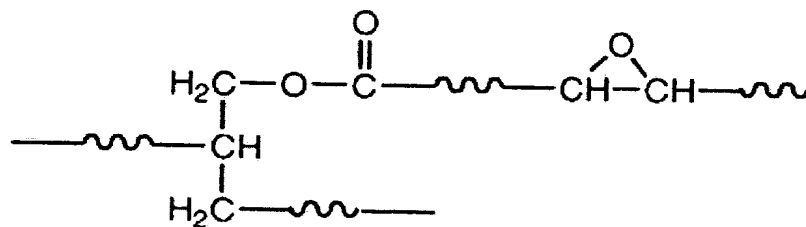
20 A particularly preferred use of these novel carbonated products is as a reaction product
21 for forming a nonisocyanate polyurethane network, such as by mixing (1) a carbonated vegetable
22 oil (such as CSBO, etc.,) and (2) an amine having functionality of at least two. Most preferably,
23 the carbonated vegetable oil and amine are mixed stoichiometrically at or within nearly balanced
24 stoichiometry, preferably within $\pm 15\%$ of balanced stoichiometry. Preferred examples of
25 amines having functionality of at least two are, e.g., ethylenediamine (ED),
26 hexamethylenediamine (HMD), and tris(2-aminoethyl) amine (TA). Other non-mono-amines
27 may be used. Most preferably, the inventive method includes a viscous solution being produced
28 from the mixing of the carbonated vegetable oil and the amine having functionality of at least
29 two, and the viscous solution is transferred into a mold, followed by curing.

1 Notably, the present invention provides a nonisocyanate polyurethane network produced
2 from a carbonated vegetable oil.

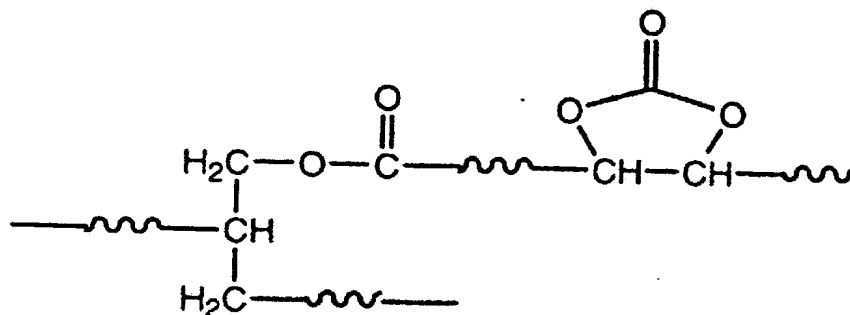
3 Nonisocyanate polyurethane networks provided by the present invention may be useful
4 for, e.g., rigid foams; flexible foams; automotive application, such as for bumpers, dashboards,
5 seating, trim components, truck beds and repair putty; construction applications, such as concrete
6 additives, flooring and crack barriers; marine applications, such as decking; consumer products,
7 such as appliances, footwear, furniture, toys; etc., and other applications for nonisocyanate
8 polyurethane networks and elastomeric materials.

9 Advantageously, the reaction described above for carrying out aspects of the present
10 invention may be conducted at atmospheric pressure.

11 Reference is now made to a particularly preferred embodiment of the present invention, in
12 which there is synthesized an SBO containing cyclic carbonate moieties, i.e., a carbonated
13 soybean oil (CSBO). For such synthesis, the starting material is an SBO having pendant epoxide
14 groups, i.e., ESBO, a commercially available material of the following basic repeating structure.



26 The invention provides for reaction of ESBO with carbon dioxide (supplied in gaseous
27 form), converting ESBO to CSBO. The repeating unit for the novel CSBO product is shown
28 below:
29



CSBO

It will be appreciated that CSBO is one example of a novel product according to the invention, and that other novel carbonated vegetable oils include the cyclic carbonate group as seen in the formula for CSBO while having different respective chains.

The novel CSBO product may according to the present invention be reacted with a polyamine (of amine functionality two or higher) to obtain a nonisocyanate polyurethane (NIPU) network, such as where the polyamines may react with the carbonate moiety on two different chains or with two different carbonate moieties on the same chain. An amine of functionality two or higher includes any amine which is not a mono-amine.

Without the invention being limited to the following Example, The following Experimental Example relates to making and CSBO, and to using CSBO to make a nonisocyanate polyurethane product.

EXPERIMENTAL EXAMPLE

Materials

Epoxidized soybean oil (Paraplex G-62) with a molecular weight of ca. 1000 g/mol and an oxygen content of 6.8% (~4.2 epoxy groups per triglyceride molecule) was provided by C.P. Hall Co. Carbon dioxide was purchased from Air Products and was used after passage through a Drierite column. Tetrabutylammonium bromide (TBAB), sodium iodide, lithium bromide,

benzyltrimethylammonium bromide, Amberlit IR 400(Cl), ethylenediamine (ED), hexamethylenediamine (HMD), and tris(2-aminoethyl)amine (TA) were purchased from Aldrich. Amines were used as received or distilled over KOH prior to use, FTIR spectra were recorded on a Nicolet 510 FT-IR spectrometer. ^1H and ^{13}C -NMR spectra were recorded on a Varian Inova 400 (400 MHz) spectrophotometer using tetramethylsilane as an internal standard. GPC profiles were obtained with a Waters SEC equipped with an autosampler 410 RI detector eluted with THF at 40° C calibrated by polystyrene standards. Viscosity measurements were made at ambient temperature using cone and plate geometry over a shear rate range of 0 to 75 s⁻¹ using an AR-1000 Rheometer from TA Instruments. Thermal stabilities of ESBO and CSBO were characterized using TGA (Model SSC 5200, Seiko) while air purging using a heating rate of 3°C/min over the temperature range of ca. ambient to 500°C.

Synthesis

Reaction of epoxidized soybean oil (ESBO) with carbon dioxide

ESBO (200 g) and dried tetrabutylammonium bromide (13.52 g; 5 mol% with respect to epoxy groups) was placed in a 500-mL flask equipped with a gas dispersion inlet tube and an outlet. The reaction mixture, while stirred magnetically, was heated to ~110°C, at which point almost all of the catalyst dissolved. A medium flow of CO₂ was then introduced. While the temperature and CO₂ flow were maintained, the level of reaction was monitored by IR spectroscopy of small aliquots taken at 5-h intervals. As the absorbance band due to formation of the cyclic carbonate moiety appeared and increased in intensity at 1805 cm⁻¹, the oxirane C-O twin bands at 823 and 845 cm⁻¹ decreased and disappeared. The reaction was complete in about 70 h. The catalyst was completely removed by dissolving the reaction mixture in ethyl acetate and extracting twice with water. The organic layer was then dried over molecular sieves and the solvent was evaporated to give 221 g (94% yield) of the clear light-brown carbonated soybean oil with a viscosity of 13,200 cps at 25°C.

Reaction of carbonated soybean oil with *n*-butylamine (model reaction)

n-Butylamine (5.85 g) was added to CSBO (11.76 g) dissolved in THF (8 mL). The solution was stirred at room temperature and the extent of reaction was followed by IR spectroscopy. While the absorbance band due to cyclic carbonate moiety at 1805 cm^{-1} diminished and finally disappeared, new bands due to the urethane C=O, -NH, and -OH groups appeared at 1704 , 1545 , and 3332 cm^{-1} , respectively. The reaction was complete after 12 h. The mixture was then dissolved in chloroform and extracted twice with slightly acidic aqueous solution. The organic layer was separated and dried, and the solvent was evaporated to give 13.5 g (92% yield) of an olive-oil-colored product.

Preparation of NIPUs

To lower the viscosity, CSBO (11.76 g) was placed in a small beaker and was heated to 60°C in a constant-temperature oven. ED (1.20 g) was then added and mixed thoroughly. The viscous solution was poured into a small mold, covered, and heated at 70°C for 10 h and then at 100°C for 3 h to give a light-brown, transparent, and flexible polymeric material of 4 mm thickness. The same procedure was followed for experiments utilizing different ratios of CSBO/ED and also when HMD or TA was used as a di- or trifunctional amine, respectively.

Characterization of NIPUs

Solvent extraction

Thin sliced samples were extracted using toluene as a solvent at room temperature for 24 h. Equilibrium swelling was achieved under these conditions. Drying of the extracted sample was performed under vacuum (30 mmHg) at 100°C for 12 h. The sol fraction, the mass difference before and after solvent extraction, was expressed in weight percentage normalized to the original dry sample mass. Three samples were used for each test and the results were

1 averaged.

3 Dynamical mechanical analysis

5 Dynamical mechanical analysis (DMA) operated in the tensile mode was carried out
6 using a Seiko DMA 210 model over the temperature range of -110 to ca. 200°C. Data were
7 obtained at a heating rate of 3°C/min at 1 Hz. In all cases, the cross-sectional areas of samples
8 were maintained as $3.0 \pm 0.5 \text{ mm}^2$. The grip-to-grip distance was 10 mm.

10 Tensile tests

12 For mechanical property testing, the samples were cut with a die into 2.54-mm-wide dog-
13 bone-shape-strips. The grip-to-grip distance was 10 mm, and the thickness of samples was
14 maintained at ca. 4.0 mm. Tests were made at ambient temperature using a constant crosshead
15 speed (5.0 mm/min) on an Instron (Model 4400R) device with a load capacity of 100 N. The
16 samples were gripped with pneumatically operated clamps.

18 EXPERIMENTAL RESULTS AND DISCUSSION

20 Reaction of ESBO with carbon dioxide

22 Epoxidized soybean oil (ESBO) (Paraplex G-62) with an average epoxy content of 4.2
23 per triglyceride molecule was used for the reaction with carbon dioxide. The reaction according
24 to Figure 7(a) was performed neat at $\sim 110^\circ\text{C}$ with different types of catalysts such as NaI, LiBr,
25 benzyltrimethylammonium bromide, Amberlit IR 400(Cl), and TBAB. Of the catalysts
26 employed, very high conversion of ESBO to carbonated soybean oil (CSBO) was particularly
27 facilitated when a 5% molar concentration of TBAB with respect to epoxy content was used.
28 The other catalysts, being insoluble or only partially soluble, resulted in very low to medium
29 conversions.

1 The extent of the reaction was followed using IR spectroscopy by focusing on the
2 appearance of a new peak at 1805 cm^{-1} due to the carbonyl of the cyclic carbonate moieties and
3 the disappearance of the twin epoxy bands at 845 and 823 cm^{-1} (Figure 1a and Figure 1b).
4 Figure 7(b) provides the proposed mechanism for this reaction. It resembles that given for the
5 reaction of oxiranes with carbon dioxide. Kihara et al., *J Organic Chem* (1993), *supra*; Kihara et
6 al., *Bull Chem Soc Jpn* (2000), *supra*.

7 In addition, the appearance of a new peak at 153.8 ppm in the ^{13}C -NMR of the product
8 due to the $\text{C}=\text{O}$ of the cyclic carbonate confirmed the conversion of epoxy groups. The
9 conversion was almost quantitative (94%) after about 70 h. The percentage conversion could be
10 evaluated by ^1H -NMR considering the signals at about $2.70\text{--}3.00\text{ ppm}$ arising from the $-\text{CH}$
11 groups of the epoxy rings in ESBO and CSBO. The viscosity of the product at 25°C was 13200
12 cP compared to the much lower value of 450 cP for ESBO. The high value of viscosity is
13 believed to be due to the presence of the polar cyclic carbonate groups causing enhanced
14 intermolecular interactions. However, to check that no significant amount of intermolecular
15 reactions occurred resulting in oligomerization or polymerization, during conversion GPC was
16 performed on both ESBO and CSBO. Figures 2a-b show the GPC profiles and, as seen, no
17 significant change in polydispersity of the product was observed; however, its molecular weight
18 (M_n 1755 g/mol) was slightly higher than that of ESBO (M_n 1414 g/mol) as estimated by using
19 polystyrene standards.

20 Figure 3, in which the percentage mass decrease with temperature is provided, contrasts
21 the thermal behavior of the two modified soy oils (ESBO and CSBO) as obtained by TGA.
22 While there is a slight increase in mass when converting the ESBO to that of the CSBO, which
23 could influence their respective vapor pressures, the TGA profiles of these two materials suggest
24 that CSBO is more thermally stable than ESBO—particularly in the range of approximately 250--
25 375°C . In addition, the Figure 3 (inset) also shows some isothermal TGA experiments carried
26 out at four different temperatures between 150 and 300°C at 50°C intervals (note that the Y-scale
27 of the inset is in logarithmic scale.) It is noted that at 150°C , the temporal mass decrease is quite
28 insignificant for both modified soy oils, being on the order of 0.1% for the time interval studied.
29 However, for the high temperature range, there is a more significant mass decrease in the time

1 interval with ESBO than for CSBO.

2 3 **Reaction of CSBO with carbon *n*-butylamine (model reaction)**

4
5 As a model, the reaction of CSBO with *n*-butylamine was performed to show the ring
6 opening of cyclic carbonate moieties and the formation of β -hydroxyurethane systems on the
7 triglyceride molecule (see Figure 7(b)). The extent of reaction was monitored by IR spectroscopy
8 (Figure 1c). The formation of new bands at 1704 and 1545 cm^{-1} due to urethane linkages as well
9 as a band at 3332 cm^{-1} due to hydroxyl groups and disappearance of the peak at 1805 cm^{-1} of
10 cyclic carbonate moieties confirmed the conversion of cyclic carbonate into the β -
11 hydroxyurethane systems in the triglyceride molecule. The absorbance bands due to the ester and
12 urethane groups overlap to some extent. No amide I band was observed in the IR spectrum of the
13 product, which showed that no transamidation reaction occurred. This was in accordance with
14 what Endo and coworkers reported for the formation of polyhydroxyurethanes. Kihara et al., J
15 Polym Sci A (1993), supra; Steblyanko, supra.

16 In addition, the disappearance of the peak at 153.8 ppm in the ^{13}C -NMR spectrum of the
17 product due to the C=O of the cyclic carbonate and the appearance of a new peak at 157 ppm of
18 C=O of the urethane groups also confirmed the formation of the urethane moieties.

19 20 **Preparation of nonisocyanate polyurethane networks**

21
22 Preparation of nonisocyanate polyurethane network materials was easily performed by
23 thoroughly mixing the equivalent weights of CSBO and ED, HMD, or TA at 60°C, pouring the
24 viscous solution into a small mold, and subsequently curing. CSBO was heated up to about 60°C
25 to reduce the viscosity to an extent that mixing became possible.

26 27 **Characterization of nonisocyanate polyurethane networks**

28
29 Solvent extraction experiments

1 Sol fraction, as a function of the molar ratio of the amine functionality of ED to cyclic
2 carbonate, is shown in Figure 4. Also included are two other data points which arise from the
3 networks made from an equal molar ratio of the amine functionality to cyclic carbonate for either
4 HMD or TA. Throughout the swelling tests, all samples maintained their shape integrity,
5 indicating that the network reaction had distinctly achieved the gel point. It is clear that the sol
6 fraction decreases at first, with the addition of ED and reaches a minimum at the stoichiometric
7 balance. With further increases in ED content, the sol fraction again increases since there is a
8 further offset again in stoichiometry. From this, it can be inferred that at the stoichiometric
9 balance, the corresponding nonisocyanate polyurethane network provides the “best” network
10 structure possessing the least amount of solubles and dangling chain ends.

11 The higher functionality amine, TA, shows an even lower amount of sol fraction at the
12 stoichiometric balance point, which is readily understood from the fact that TA will contribute to
13 promote a tighter network structure than the equivalent diamine moieties. The longer chain and
14 more flexible diamine, HMD, exhibited a slightly lower sol fraction compared with ED.

15 DMA results

16
17
18 In Figures 5A and 5B, the DMA parameters of $\tan \delta$ and E' are shown as a function of
19 temperature, respectively. The principal peak temperature, which is apparent in the $\tan \delta$ results,
20 is distinctly assigned to the glass transition of the corresponding network. For the series with
21 varying ED content, it is noted that the T_g systematically increases with ED addition, up to the
22 stoichiometric balance, but then again decreases with further ED concentration. The overall
23 thermal window of T_g variation with ED content is also noted to be about 20°C.

24 In addressing the two remaining data points associated with the triamine, TA, as well as
25 the second diamine HMD, it is noted that the TA-based network provided the highest T_g value of
26 approximately 43°C, whereas the HMD network exhibited the lowest T_g at stoichiometric
27 balance at approximately 18°C. For clarity, the variation of the T_g 's, as determined by $\tan \delta$, are
28 presented in the Figure 5A inset for all samples. These results regarding T_g are clearly consistent
29 with respect to the earlier sol fraction behavior in that, the nearer the stoichiometric balance, the

1 higher the T_g will be for those systems with varying ED, and in addition, the triamine, TA, again
2 provides the highest glass transition temperature, indicative of the fact that it has a tighter
3 network than that of either the ethylene or the hexamethylene diamine-based networks. Of note
4 is also the fact that the HMD-based network gives a somewhat lower T_g than the corresponding
5 ED containing sample, which may be considered in view of the higher level of flexibility of the
6 HMD moiety. Finally, another interesting observation relating to the T_g behavior is that the
7 intensity of the glass transition, as denoted by the tan δ value at its peak, decreases in the order of
8 HMD > ED > TA. This ordering is the reverse of the ordering of the T_g's of these same
9 respective three stoichiometrically balanced samples.

10 It is also noted that, in Figure 5B, there is a relatively broad and weak secondary loss peak
11 that occurs at about -50°C for some of the samples. This small relaxation peak may not be real
12 but rather may be associated with instrumental artifacts.

13 In addressing the storage modulus data given in Figure 5B, it is noted that its behavior
14 above the respective T_g of a given sample shows that the TA-based urethane network displays
15 the highest rubbery plateau modulus, consistent with its higher level of cross-link density (lowest
16 solubles) as well as its higher T_g. The samples showing the variation in ED content illustrate
17 that the highest rubbery modulus occurs at stoichiometric balance and is lower for any other
18 composition irrelevant of whether it is the diamine or the cyclic carbonate moiety that is in
19 excess. The HMD-based network exhibited the second highest rubbery plateau modulus relative
20 to all other networks studied. Specifically, it was below the network made from TA but above all
21 of those based on ED. While it was noted above that the more flexible HMD gave rise to a lower
22 T_g than the stoichiometrically balanced networks based on TA and ED, its rubbery plateau
23 modulus need not necessarily be the lowest of the three. In fact, it is noted that the ordering of
24 the rubbery plateau moduli for the three stoichiometrically balanced networks is inversely related
25 to the sol fraction.

26 27 Tensile testing results

28
29 The results of the tensile experiments performed under room conditions are noted in

Figure 6. The results confirm that the TA-based network displays the highest level of stress for a given strain when compared against the other two stoichiometric balanced materials formulated with either ED or HMD. In addition, the HMD-based network displays the lower modulus of the same three systems even though the rubbery plateau modulus of the HMD network is intermediate to that of the TA and ED networks. This result is simply due to the fact that the HMD material possesses the lower T_g, which promotes a lower modulus at ambient temperature where the tensile tests were conducted (see Figure 5B). Finally, it is particularly noted that, for the stoichiometric balance of ED with the CSBO moiety, the stress-strain behavior is higher than for all other compositions of ED with the results being consistent with the solubles data obtained by extraction and the DMA glass transition results. See also the Figure 6 (inset), which shows the levels of stress at 120% strain for the samples containing ED. The strain at break for all of the ED-based networks is nearly constant at approximately 150%, thereby showing no systematic dependence on the ratio of ED to that of CSBO. In contrast, the strain at break for the tighter network TA-based material is distinctly lower (approximately 70%) and therefore well below that of any of the ED- or HMD- (170%) based urethanes.

Conclusions from Experiment

Reaction of epoxidized soybean oil with carbon dioxide under atmospheric pressure using tetrabutylammonium bromide as a catalyst to prepare carbonated soybean oil was confirmed. Further, CSBO easily reacts with di- or triamines to produce nonisocyanate polyurethane networks.

Extractables characterization from the various NIPUs made from the three different amines confirmed that all network reactions had easily reached the gel point, since sample integrity was maintained for all materials of equilibrium swelling in toluene. DMA and tensile tests were in harmony with the extractable results in that, as extractable level increased for a given type of amine reactant, T_g and stress at a given strain increased. By varying the stoichiometric balance of the reactant ED with that of the cyclic carbonate moiety, it was confirmed that, as the stoichiometric balance was approached, the level of extractables decreased,

1 while the stress at a given strain and the corresponding network Tg increased. Very consistently,
2 and regardless of the type of the tests employed, the samples made from triamine showed the
3 lowest soluble fraction (6.8%), the smallest strain at break, E_b (170%). When the amount of ED
4 was varied among samples, the equivalent weight sample carried the lowest soluble fraction
5 (10.7%), the highest Tg (ca. 34°C), and the highest level of stress among themselves. Strain at
6 break for the samples made from ED were approximately constant regardless of the amount of
7 ED (ca. 150%).
8

9 The Experiment described above is exemplary, and the invention is not limited thereto. It
10 will be appreciated that the epoxide ring to be reacted with carbon dioxide may be an epoxide
11 ring included, by way of one example, in an ESBO as discussed above in the Experiment, or
12 included in another derivatized natural resource, such as another vegetable oil; an animal oil; etc.
13 The present invention advantageously provides for making a nonisocyanate polyurethane (NIPU)
14 from a vegetable oil or another renewable natural resource.

15 While the invention has been described in terms of its preferred embodiments, those
16 skilled in the art will recognize that the invention can be practiced with modification within the
17 spirit and scope of the appended claims.